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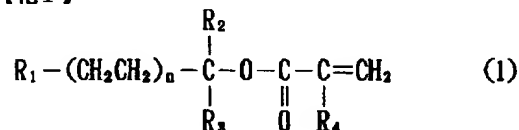
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(54) 【発明の名称】 ポリエチレンマクロモノマーおよびその製造法

(57) 【要約】

【構成】 炭素数1から6の直鎖または分岐のアルキルリチウム／3級ジアミン系開始剤を用いてエチレンをリビング重合させ、これに所定のカルボニル化合物を反応させ、又は酸素酸化させ、さらに(メタ)アクリル酸ハライドを反応させることにより、次式で表されるポリエチレンマクロモノマーを得る。

【化1】



(式中、R₁は炭素数1から6の直鎖又は分岐の飽和炭化水素基、R₂、R₃は水素又は炭素数1～18の脂肪族若しくは芳香族炭化水素基、R₄は水素又はメチル基、nは10～1000の整数であり、R₁～R₃は同一でも異なっても良い。)

【効果】 (メタ)アクリロイル基を末端に有する新規なポリエチレンマクロモノマーを高収率かつ高純度で得

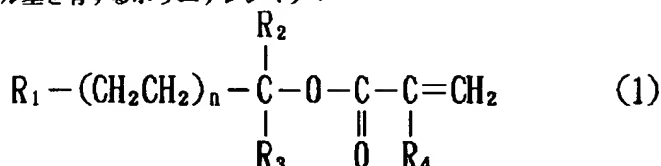
ることができる。これは他の様々なビニルモノマーと共重合して、ポリマーブレンド用相溶化剤、表面改質剤等に好適な構形グラフトポリマーを合成するのに用いることができる。

【特許請求の範囲】

【請求項1】 次式(1)で表される、末端にアクリロイル基又はメタクリロイル基を有するポリエチレンマク*

*ロモノマー。

【化1】



(式中、R₁は炭素数1から6の直鎖又は分岐の飽和炭化水素基、R₂、R₃は水素又は炭素数1～18の脂肪族若しくは芳香族炭化水素基、R₄は水素又はメチル基、nは10～1000の整数であり、R₁～R₃は同一でも異なっても良い。)

【請求項2】 1) 炭素数1から6の直鎖又は分岐のアルキルリチウム/3級ジアミン系開始剤を用いてエチレンをリビング重合させる段階と、

2) 次式(2)で示されるカルボニル化合物を反応させる段階、及び

【化2】



(式中、R₂及びR₃は独立に水素又は炭素数1から18の脂肪族若しくは芳香族炭化水素である。)

3) アクリル酸ハライド又はメタクリル酸ハライドを反応させる段階とからなる、末端にアクリロイル基又はメタクリロイル基を有するポリエチレンマクロモノマーの製造法。

【請求項3】 1) 炭素数1から6の直鎖又は分岐のアルキルリチウム/3級ジアミン系開始剤を用いてエチレンをリビング重合させる段階と、

2) 酸素酸化を行う段階、及び

3) アクリル酸ハライド又はメタクリル酸ハライドを反応させる段階とからなる、末端にアクリロイル基又はメタクリロイル基を有するポリエチレンマクロモノマーの製造法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は、(メタ)アクリロイル基、即ちアクリロイル基又はメタクリロイル基を分子末端に有するポリエチレンマクロモノマーおよびその製造法に関する。

【0002】

【従来の技術】 ポリエチレンはコスト的、機械的等の特性に優れ、様々な樹脂製品の原料として最も幅広く用いられている。このようにポリエチレンが成形材料として広く用いられている理由としては、ポリエチレンが化学的に安定であることが挙げられる。

10※【0003】 しかしながらこの化学的安定性は、成形時および製品の物性に関しては長所であるのに対して、高い機能を必要とされる際に化学的に変性を施そうとする試みに対しては妨げとなっている。この欠点を補い、ポリエチレンに機能性をもたせる方法として、例えば、高圧法により酢酸ビニル、メタクリル酸エステル等の極性モノマーと共重合する方法、或いは既存のポリエチレンに対し、過酸化物の存在下に無水マレイン酸等の極性モノマーをグラフト重合する方法等が知られている。しかしながら、高圧共重合法によっては低密度ポリエチレンの変性体しか得られず、またグラフト重合法ではホモポリマーが副生したり変性量の制御が困難であるなど、構造を自在に制御した変性ポリエチレンを得ることは一般に困難であった。

【0004】

【発明が解決しようとする課題】 ところで、構造の制御されたグラフトポリマーの製造法として、Milkovichらによって用いられたマクロモノマー法がある(R. Milkovich, ACS Symp. Ser., 166, 41 (1981))。マクロモノマーは末端に重合可能基を持ったポリマー或いはオリゴマーであり、様々なビニルモノマーと共重合することによって、いわゆる櫛形のグラフトポリマーを合成することができる。このグラフトポリマーは高分子材料の表面改質剤、或いは他の高分子との複合化の際の相溶化剤として用いることができる。

【0005】 しかしながら、ポリエチレンマクロモノマーに関する報告は無く、汎用性の高いポリエチレン改質のためのマクロモノマーが必要とされている。

【0006】

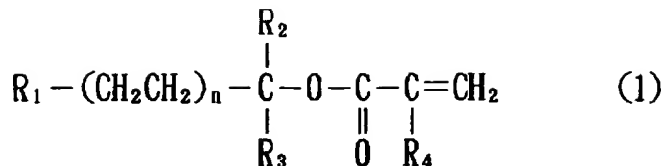
【課題を解決するための手段】 かかる実状において本発明者らは、ポリエチレンマクロモノマーを開発すべく鋭意検討の結果、リビングポリエチレンを特定のカルボニル化合物と反応させ、或いは酸素酸化により合成したポリエチレンアルコキシドに、アクリル酸ハライド又はメタクリル酸ハライドを反応させる方法を見出し、表記の新規化合物を得ることに成功したものである。

【0007】 即ち本発明は、以下に示す新規なポリエチレンマクロモノマーおよびその製造法を提供する。

1. 次式(1)で表される、末端に(メタ)アクリロイル基を有するポリエチレンマクロモノマー。

※50 【0008】

【化3】



【0009】(式中、 R_1 は炭素数1から6の直鎖又は分岐の飽和炭化水素基、 R_2 、 R_3 は水素又は炭素数1～18の脂肪族若しくは芳香族炭化水素基、 R_4 は水素又はメチル基、 n は10～1000の整数であり、 R_1 ～ R_3 は同一でも異なっても良い。)

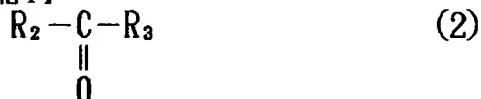
2. 以下の工程からなる、末端に(メタ)アクリロイル基を有するポリエチレンマクロモノマーの製造法。

1) 炭素数1から6の直鎖又は分岐のアルキルリチウム／3級ジアミン系開始剤を用いてエチレンをリビング重合させる段階と、

2) 次式(2)で示されるカルボニル化合物を反応させる段階、及び

【0010】

【化4】



【0011】(式中、 R_2 及び R_3 は独立に水素又は炭素数1から18の脂肪族若しくは芳香族炭化水素である。)

3) (メタ)アクリル酸ハライドを反応させる段階。

【0012】3. 以下の工程からなる、末端に(メタ)アクリロイル基を有するポリエチレンマクロモノマーの製造法。

1) 炭素数1から6の直鎖又は分岐のアルキルリチウム／3級ジアミン系開始剤を用いてエチレンをリビング重合させる段階と、

2) 酸素酸化を行う段階、及び

3) (メタ)アクリル酸ハライドを反応させる段階。

【0013】以下に本発明をさらに詳しく説明する。本発明による、末端に(メタ)アクリロイル基を有するポリエチレンマクロモノマーは、アクリロイル基又はメタクリロイル基の結合する炭素の一つまたは二つの炭化水素置換基を有する。かかる炭化水素置換基としては炭素数1～18の脂肪族または芳香族炭化水素基が含まれる。18より多い炭素数のものを用いることも原理的には可能であるが、原料の入手性、生成するポリエチレンの物性、反応性等を考慮すれば実用的ではない。

【0014】脂肪族炭化水素置換基の具体例としては、メチル基、エチル基、*n*-プロピル基、*i*-プロピル基、*n*-ブチル基、*i*-ブチル基、*sec*-ブチル基、*tert*-ブチル基、 $C_5 \sim C_{18}$ の直鎖または分岐の飽

* 和炭化水素基、脂環式炭化水素基等が挙げられる。なお特殊な場合として、二つの置換基が共有結合で結ばれ、(メタ)アクリロイル基と結合する炭素原子を含む炭化水素環が形成されているものも本発明の範囲にある。かかる炭化水素環の具体例としては、シクロペンタン環、シクロヘキサン環等が挙げられる。

【0015】芳香族炭化水素置換基の具体例としては、フェニル基、メチルフェニル基、エチルフェニル基、ナフチル基等が挙げられる。

【0016】例えば立体的に嵩高い置換基は反応性を低下させる傾向があり、これらの置換基はポリエチレンマクロモノマーの重合反応性に影響を与える。

20 【0017】本発明の末端に(メタ)アクリロイル基を有するポリエチレンマクロモノマーは、反対側の末端に炭素数1から6の直鎖又は分岐の飽和炭化水素基を有する。即ちメチル基、エチル基、*n*-ブチル基などであり、短鎖分岐の具体例としては、2-メチル基、3-メチル基、2, 2-ジメチル基等が挙げられる。これらの末端の分岐鎖は、生成ポリエチレンの物性に対し、その重合度が低い場合には融点を低下させるなどの変化を発現するが、重合度が高い場合は何等影響を及ぼさない。

【0018】本発明の末端に(メタ)アクリロイル基を有するポリエチレンマクロモノマーは、エチレン繰返し単位として10～1000の範囲の重合度を有する混合物である。その重合度分布に特に制限はないが、通常は1.05～5程度である。重合度が概ね300以下の場合には生成ポリエチレンマクロモノマーはワックス様の、それ以上ではプラスチック様の外観および物性を示す。

【0019】次に、本発明の末端に(メタ)アクリロイル基を有するポリエチレンマクロモノマーの製造法について説明する。まず第一段階として、炭素数1から6の直鎖または分岐のアルキルリチウム／3級ジアミンによるエチレンのリビング重合を行う。

【0020】ポリエチレンのリビング重合においては、非極性の脂肪族炭化水素溶媒が用いられる。かかる溶媒の具体例としては、ペンタン、ヘキサン、ヘプタン、オクタン、シクロヘキサン、シクロペンタン等が挙げられる。好ましくはシクロヘキサンである。

【0021】炭素数1から6の直鎖または分岐のアルキルリチウム化合物としては、メチルリチウム、エチルリチウム、*n*-ブチルリチウム、*s*-ブチルリチウム、*t*-ブチルリチウム等が用いられる。ここで用いるリチウ

ム化合物の有機基が、生成するポリエチレンの一方の末端に導入されることになる。

【0022】3級ジアミンとしては、二つの窒素間の原子数が2ないし3個のものが好適に用いられる。かかるジアミンの具体例としては、テトラメチルエチレンジアミン、ジピペリジノエタン、ジピロリジノエタン、スバルテイン等が挙げられる。

【0023】これらの3級ジアミンは通常、アルキルリチウムに対して0.1~10当量用いられる。3級ジアミンの使用量が0.1当量より少ないと重合が遅く、また有機基導入反応の収率が低くなり、10当量より多いとリビング末端が失活してしまうものが多くなる。

【0024】上記のアルキルリチウム化合物および3級ジアミンを含む炭化水素溶液にエチレンを導入することで、エチレンのリビング重合が進行する。エチレンの導入圧力に特に制限はないが、 $1\text{kg}/\text{cm}^2 \sim 100\text{kg}/\text{cm}^2$ が適当である。 $1\text{kg}/\text{cm}^2$ より低い場合には重合反応が遅すぎて、経済的ではない。他方、 $100\text{kg}/\text{cm}^2$ を超える高压においては重合が速すぎて、反応の制御が困難となる。

【0025】重合は $0^\circ\text{C} \sim 100^\circ\text{C}$ で好適に行われる。望ましくは $20^\circ\text{C} \sim 80^\circ\text{C}$ である。反応温度が 0°C より低いと重合反応が遅くなり過ぎ、また生成するポリエチレンが沈澱しやすくなるため好ましくない。他方、反応温度が 100°C を越えたとリビング末端が失活しやすくなるため好ましくない。

【0026】重合時間は、重合温度、3級ジアミン濃度、エチレン導入圧力等によって異なるが、一般に0.1時間から24時間程度である。重合時間を変化させることにより、生成するポリエチレンの分子量を制御することができる。リビング末端の失活を防ぐ点から、重合熱を除去できる限り、重合時間はなるべく短時間であることが好ましい。

【0027】第二段階として、上記方法により生成したリビング末端にカルボニル化合物を反応させる。カルボニル化合物としては特定のアルデヒド、ケトンが用いられ、目的とする末端構造に応じて適宜使い分けられる。アルデヒドを用いる場合は1級又は2級の、ケトンを用いる場合は3級のリチウムアルコキシドが導入されることになる。かかるアルデヒド、ケトンとしては、炭素数1~18の脂肪族または芳香族炭化水素基を有するものが用いられる。

【0028】通常、アルキルリチウムのカルボニル化合物への求核付加反応は α 水素の引き抜き反応と競合するため、ある程度の割合で末端官能基を持たないポリエチレンを副生する。カルボニル基に隣接したメチル基を有するケトン類を用いる場合、反応条件にもよるが、末端導入反応率は50~70%程度に留まる。かかるケトン類の具体例としては、アセトン、2-ブタノン、2-ペンタノン、3-メチル-2-ブタノン、アセトフェノン

等が挙げられる。カルボニル基に隣接した基がメチル基以外でかつ α 水素を有するケトンにおいては引き抜き反応が遅くなるため、有機基の導入率は向上し、70~90%に達する。かかるケトンの具体例としては、3-ペンタノン、シクロペンタノン、シクロヘキサノン等が挙げられる。一方、ケトンよりも立体障害の少ないアルデヒド類においては、 α 水素があってもほぼ定量的に目的の水酸基等含有ポリエチレンを得ることができる。かかるアルデヒドの具体例としては、プロパナール、ブタナール、ペンタナール、ヘキサナール等が挙げられる。 α 水素を持たないカルボニル化合物においては、ほぼ定量的に有機基が導入される。かかるカルボニル化合物の具体例としては、ホルムアルデヒド、ベンズアルデヒド、ベンゾフェノン等が挙げられる。これらのカルボニル化合物及びアルデヒド類においては、90%を越える導入率を得ることが可能である。

【0029】カルボニル化合物の量に特に制限はないが、極めて定量的な反応であるから、リビング末端に対し等モル量ないし1.2倍の過剰モル量程度で十分である。過剰のカルボニル化合物の使用は、カニッツアロ反応、アルドール縮合等の副反応を生ずるので好ましくない。

【0030】カルボニル化合物とリビングポリエチレンとの反応は均一系においては室温でもほぼ1分以内に完結する。しかしながら、ポリエチレンの分子量が高く沈澱を生成している場合には、数分~数時間の反応が必要となる。反応温度に特に制限はないが、通常 $0^\circ\text{C} \sim 100^\circ\text{C}$ 、好ましくは $20^\circ\text{C} \sim 80^\circ\text{C}$ で行われる。一般には、重合に用いた温度と同一の温度において行われる。カルボニル化合物の添加方法については特に限定しないが、発熱を伴うことから微量ずつ加えるか、重合に用いられる炭化水素溶媒で希釈してから加えることが望ましい。

【0031】本発明の末端に(メタ)アクリロイル基を有するポリエチレンマクロモノマーの製造法においては、第二段階として、上記の如きカルボニル化合物との反応に代えて、リビング末端の酸素酸化を行うことも可能である。具体的には所定の分子量に達したリビングポリエチレンを含む反応器内のエチレンガスを除去した後、酸素を導入することで達成される。反応条件によっては、窒素、アルゴン等の不活性ガスで適当な濃度に希釈された酸素を用いて、反応速度を調節することが望ましい。一般にはこの酸素酸化は、乾燥空気を導入することにより達成される。酸素(混合)ガスの導入速度および圧力は、反応速度が制御できる範囲であれば特に制限されない。過酸化物の生成を防ぐためには、微量ずつ導入することが好ましい。酸素酸化反応を行う際の温度についても特に制限はないが、通常 $-78^\circ\text{C} \sim 100^\circ\text{C}$ 、好ましくは $-30^\circ\text{C} \sim 70^\circ\text{C}$ である。

【0032】第二段階までで生成したポリエチレンは、

分子末端にリチウムアルコキシドを有しているが、次に第三段階として、上記の方法で得られたポリエチレンの分子末端に(メタ)アクリル酸ハライド即ちアクリル酸又はメタクリル酸を反応させる。加える(メタ)アクリル酸ハライドの量に特に制限はないが、アルコキシド末端に対して1から1.2倍モル当量程度でよい。この反応は、カルボニル化合物とアルキルリチウムとの反応に比べると遅いものの、室温以上では数分以内に完結する。しかしながら、アルコキシドの分子量が非常に大きくなった場合には、数時間～数日の反応を必要とする。反応温度に特に制限はないが、通常は0℃～100℃、好ましくは20℃～80℃で行われる。一般には前反応で用いた温度と同一か、やや高温で行われる。

【0033】

【発明の効果】本発明により、(メタ)アクリロイル基を末端に有する新規なポリエチレンマクロモノマーを高収率かつ高純度で得ることができる。本発明で得られるポリエチレンマクロモノマーは、ほとんど全ての分子末端に一つずつ(メタ)アクリロイル基を有することから、他の様々なビニルモノマーと共重合することにより、樹形グラフトポリマーを合成することができる。また、このグラフトポリマーは、ポリマーブレンド用相溶化剤、表面改質剤等に好適に用いられる。

【0034】

【実施例】以下に実施例を用いて本発明を更に詳しく説明する。

実施例1

窒素置換した1リットルのオートクレーブ中に、乾燥シクロヘキサン400ml、テトラメチルエチレンジアミン3ml、n-ブチルリチウム(1.6mol/リットル)12.5mlを仕込み、30℃にてエチレングスを2kg/cm²の圧力で導入した。30分重合を行った後、エチレングス

を除去して窒素置換し、そこへベンズアルデヒド2.2mlを滴下した。30℃にて5分間反応させた後、メタクリル酸クロリド2.2mlを滴下した。30℃にて15分間反応させた後、オートクレーブを明け、内容物を2リットルのメタノール中に投入した。1時間攪拌した後、減圧濾過にて生成した固体を集め、50℃のオーブンで真空下に24時間乾燥し、白色固体を得た。生成物の収量は13.0g、Waters社製の装置を用いたGPC分析(オルトジクロロベンゼン、135℃、ポリエチレン標準サンプルで校正)の結果、生成物の数平均分子量は730であった。

【0035】¹H-NMR分析(Bruker社製、200MHz、テトラクロロエチレン、80℃。ロック溶媒としてDMSO-d₆を二重管で用い、外部標準としてTMSを用いた。)の結果、0.8ppm(トリプレット)に開始末端メチル基、1.2ppm付近に主鎖のメチレン基、2.0ppm(ダブルダブレット)にメタクリロイル基のメチル、5.5および6.2ppmにメタクリロイル基のビニル、5.8ppm(トリプレット)にベンジル位メチン、7.2ppm付近にフェニル基のシグナルが観察された。各々のシグナルの積分比から、末端メタクリロイル基導入率は87%であることがわかった。

【0036】実施例2

実施例1と同様の方法でエチレンの重合を行った後、エチレングスを除去し、乾燥空気で置換した。30℃にて10分間酸化反応を行った後、メタクリル酸クロリド2.2mlを添加し、15分間反応させた。実施例1と同様に後処理を行い、白色固体12.8gを得た。数平均分子量は670(実施例1と同様のGPC)、末端メタクリロイル基導入率は80%(実施例1と同様の¹H-NMR)であった。

PATENT ABSTRACTS OF JAPAN

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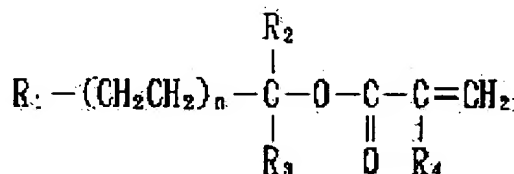
AMIYA TSUYOSHI

(54) POLYETHYLENE MACROMONOMER AND ITS PRODUCTION

(57)Abstract:

PURPOSE: To produce, in a high yield, a new high-purity polyethylene macromonomer which has a terminal (meth)acryloyl group and can be copolymerized with another vinyl monomer to give a comb-type graft polymer suitable as a polymer blend compatibilizer, a surface modifier, etc.

CONSTITUTION: Ethylene is subjected to living polymn. using a 1-6C linear or branched alkylolithium/tert. diamine initiator, reacted with a specific carbonyl compd. or oxidized with oxygen and reacted with a (meth)acrylic acid halide to give a polyethylene macromonomer of the formula (wherein R1 is a 1-6C linear or branched satd. hydrocarbon group; R2 and R3 are each H or a 1-18C aliph. or arom. hydrocarbon group provided R1, R2, and R3 are the same or different from each other; R4 is H or methyl; and n is an integer of 10-1,000).



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the polyethylene macro monomer which has an acryloyl (meta) radical, i.e., an acryloyl radical, or a methacryloyl radical at the molecule end, and its manufacturing method.

[0002]

[Description of the Prior Art] Polyethylene is excellent in the cost property of mechanical **, and is used most broadly as a raw material of various resin products. Thus, the fact that polyethylene is chemically stable is cited as a reason polyethylene is widely used as a molding material.

[0003] However, in case a high function is needed for this chemical stability to being the advantage about the physical properties of the time of shaping, and a product, it serves as hindrance to the attempt which is going to denaturalize chemically. This fault is compensated and the approach of carrying out the graft polymerization of the polar monomers, such as a maleic anhydride, to the bottom of existence of a peroxide etc. is learned as an approach of giving functionality to polyethylene, to the approach of copolymerizing with polar monomers, such as vinyl acetate and methacrylic ester, with a high pressure process, or existing polyethylene. however, only the denaturation object of low density polyethylene is acquired depending on a high-pressure copolymerization method -- not having -- moreover, a graft polymerization method -- if -- control of the amount of denaturation is difficult in a homopolymer carrying out a byproduction -- etc. -- generally it was difficult to obtain the denaturation polyethylene which controlled structure free.

[0004]

[Problem(s) to be Solved by the Invention] By the way, there is the macro monomer method used by Milkovich and others as a manufacturing method of the graft polymer by which structure was controlled (R.Milkovich, ACS Symp.Ser., 166, and 41 (1981)). A macro monomer is the polymer or oligomer which had a polymerization possible radical in the end, and can compound the so-called graft polymer of Kushigata by copolymerizing with various vinyl monomers. This graft polymer can be used as the surface treatment agent of polymeric materials, or a compatibilizer in the case of compound-izing with other macromolecules.

[0005] However, there is no report of a polyethylene macro monomer and the macro monomer for high polyethylene reforming of versatility is needed.

[0006]

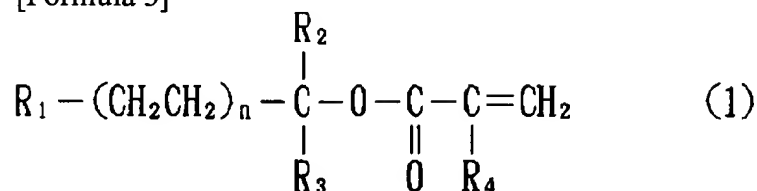
[Means for Solving the Problem] The approach of making acrylic-acid halide or methacrylic-acid halide reacting to the polyethylene alkoxide which this invention persons made living polyethylene reacting with a specific carbonyl compound wholeheartedly in this actual condition as a result of examination a polyethylene macro monomer being developed, or was compounded by oxygen acid-ization is succeeded in obtaining a header and a declared new molecular entity.

[0007] That is, this invention offers the new polyethylene macro monomer shown below and its manufacturing method.

1. Polyethylene macro monomer which is expressed with degree type (1) and which has acryloyl (meta) radical at end.

[0008]

[Formula 3]



[0009] (For R1, the straight chain of carbon numbers 1-6 or the saturated hydrocarbon radical of branching, and R2 and R3 are [hydrogen or a methyl group, and n of the aliphatic series of hydrogen or carbon numbers 1-18 or an aromatic hydrocarbon radical, and R4] the integers of 10-1000 among a formula, and even if R1-R3 are the same, they may differ.)

2. Manufacturing method of polyethylene macro monomer which has acryloyl (meta) radical at end which consists of the following processes.

1) the phase of carrying out living polymerization of the ethylene using the straight chain of carbon numbers 1-6, or the alkyl lithium / the 3rd class diamine system initiator of branching, and the phase of making the carbonyl compound shown by 2 degree type (2) reacting -- and [0010]

[Formula 4]



[0011] (R2 and R3 are the aliphatic series or aromatic hydrocarbon of hydrogen or carbon numbers 1-18 independently among a formula.)

3) (meta) Phase of making acrylic-acid halide reacting.

[0012] 3. Manufacturing method of polyethylene macro monomer which has acryloyl (meta) radical at end which consists of the following processes.

1) The phase of carrying out living polymerization of the ethylene using the straight chain of carbon numbers 1-6, or the alkyl lithium / the 3rd class diamine system initiator of branching, the phase of performing 2 oxygen-acid-ization, and the phase of making 3 (meta) acrylic-acid halide reacting.

[0013] This invention is explained in more detail below. The polyethylene macro monomer by this invention which has an acryloyl (meta) radical at the end has one or two hydrocarbon substituents to the carbon which an acryloyl radical or a methacryloyl radical combines. As this hydrocarbon substituent, the aliphatic series or the aromatic hydrocarbon radical of carbon numbers 1-18 is contained. Although it is also theoretically possible to use the thing of more carbon numbers than 18, it is not practical if the availability of a raw material, the physical properties of the polyethylene to generate, reactivity, etc. are taken into consideration.

[0014] As an example of an aliphatic hydrocarbon substituent, a methyl group, an ethyl group, n-propyl group, i-propyl group, n-butyl, i-butyl, sec-butyl, tert-butyl, the straight chain of C5-C18 or the saturated hydrocarbon radical of branching, an alicyclic hydrocarbon radical, etc. are mentioned. In addition, when special, two substituents are connected with covalent bond and some in which the hydrocarbon ring containing the carbon atom combined with an acryloyl (meta) radical is formed are [*****] in the range of this invention. A cyclopentane ring, a cyclohexane ring, etc. are mentioned as an example of this hydrocarbon ring.

[0015] As an example of an aromatic hydrocarbon substituent, a phenyl group, a methylphenyl radical, an ethyl phenyl group, a naphthyl group, etc. are mentioned.

[0016] for example, -- three-dimensional -- ** -- a high substituent tends to reduce reactivity and these substituents affect the polymerization reactivity of a polyethylene macro monomer.

[0017] The polyethylene macro monomer which has an acryloyl (meta) radical at the end of this invention has the straight chain of carbon numbers 1-6, or the saturated hydrocarbon radical of branching at the end of the opposite side. That is, it is a methyl group, an ethyl group, n-butyl, etc., and 2-methyl group, 3-methyl group, 2, and 2-dimethyl radical etc. is mentioned as an example of short-chain branch. To the physical properties of generation polyethylene, the branched chain of these ends discovers change of reducing the melting point, when the polymerization degree is low, but when polymerization degree is high, it does not do effect at all.

[0018] The polyethylene macro monomer which has an acryloyl (meta) radical at the end of this invention is mixture which has the polymerization degree of the range of 10-1000 as an ethylene repeat unit. Although there is especially no limit in the distribution of polymerization degree, it is usually 1.05 to about five. When a degree of polymerization is 300 or less in general, as for a generation polyethylene macro monomer, the plastics' appearance and physical properties are shown more than by it of Mr. Wacks.

[0019] Next, the manufacturing method of the polyethylene macro monomer which has an acryloyl (meta) radical at the end of this invention is explained. The straight chain of carbon numbers 1-6 or living polymerization of the ethylene by the alkyl lithium / 3rd class diamine of branching is first performed as a first stage story.

[0020] The aliphatic hydrocarbon solvent of a non-polarity is used in the living polymerization of polyethylene. As an example of this solvent, a pentane, a hexane, a heptane, an octane, a cyclohexane, a cyclopentane, etc. are mentioned. It is a cyclohexane preferably.

[0021] As the straight chain of carbon numbers 1-6, or an alkyl lithium compound of branching, methyl lithium, an ethyl lithium, n-butyl lithium, s-butyl lithium, t-butyl lithium, etc. are used. The organic radical of the lithium compound used here will be introduced into one end of the polyethylene to generate.

[0022] As the 3rd class diamine, 2 thru/or three things are suitably used for the atomic number between two nitrogen. Tetramethylethylenediamine, dipiperidinoethane, JIPIRORIJINO ethane, sparteine, etc. are mentioned as an example of this diamine.

[0023] 0.1-10Eq of the 3rd class diamines of such is usually used to alkyl lithium. When there is less amount of the 3rd class diamine used than 0.1Eq, a polymerization is late, and the yield of an organic radical installation reaction becomes low, and if [than 10Eq] more, that in which a living end deactivates will increase.

[0024] The living polymerization of ethylene advances by introducing ethylene into the hydrocarbon solution containing an above-mentioned alkyl lithium compound and the 3rd class diamine. Although there is especially no limit in the introductory pressure of ethylene, 1kg/cm² - 100kg/cm² is suitable. When lower than 1kg/cm², a polymerization reaction is too slow and is not economical. On the other hand, in the high pressure exceeding 100kg/cm², a polymerization is too quick and control of a reaction becomes difficult.

[0025] A polymerization is suitably performed at 0 degree C - 100 degrees C. It is 20 degrees C - 80 degrees C desirably. Since a polymerization reaction will become slow too much and the polyethylene to generate will become easy to precipitate if reaction temperature is lower than 0 degree C, it is not desirable. On the other hand, since a living end will become easy to deactivate if reaction temperature exceeds 100 degrees C, it is not desirable.

[0026] Although polymerization time amount changes with polymerization temperature, the 3rd class diamine concentration, ethylene installation pressures, etc., generally it is about 24 hours from 0.1 hours. By changing polymerization time amount, the molecular weight of the polyethylene to generate is controllable. As long as the heat of polymerization is removable from the point which prevents deactivation of a living end, as for polymerization time amount, it is desirable that it is a short time if possible.

[0027] A carbonyl compound is made to react to the living end generated by the above-mentioned approach as a second stage story. A specific aldehyde and a ketone are used as a carbonyl compound, and it is properly used suitably according to the end structure made into the purpose. When using an

aldehyde and using the ketone of the 1st class or the 2nd class, the lithium alkoxide of the 3rd class will be introduced. As this aldehyde and a ketone, what has the aliphatic series or the aromatic hydrocarbon radical of carbon numbers 1-18 is used.

[0028] Usually, the nucleophilic addition to the carbonyl compound of alkyl lithium carries out the byproduction of the polyethylene which does not have an end functional group at a certain amount of rate in order to compete with the abstraction reaction of alpha hydrogen. Although it is based also on a reaction condition when using the ketones which have the methyl group which adjoined the carbonyl group, end installation conversion is only about 50 - 70%. As an example of these ketones, an acetone, 2-butanone, 2-pentanone, 3-methyl-2-butanone, an acetophenone, etc. are mentioned. Since an abstraction reaction becomes slow in the ketone which the radical which adjoined the carbonyl group is except a methyl group, and has alpha hydrogen, the rate of installation of an organic radical improves and reaches to 70 - 90%. 3-pentanone, cyclopentanone, a cyclohexanone, etc. are mentioned as an example of this ketone. On the other hand, in aldehydes with less steric hindrance than a ketone, even if there is alpha hydrogen, content polyethylene, such as the target hydroxyl group, can be obtained almost quantitatively. Propanal, butanal, pentanal, hexanal, etc. are mentioned as an example of this aldehyde. In a carbonyl compound without alpha hydrogen, an organic radical is introduced almost quantitatively. Formaldehyde, a benzaldehyde, a benzophenone, etc. are mentioned as an example of this carbonyl compound. In these carbonyl compounds and aldehydes, it is possible to obtain the rate of installation exceeding 90%.

[0029] Although there is especially no limit in the amount of a carbonyl compound, since it is a very quantitative reaction, one 1.2 times superfluous molar quantity extent [an equimolecular amount thru/or] of this is enough to a living end. Since use of a superfluous carbonyl compound produces side reaction, such as a Cannizzaro reaction and aldol condensation, it is not desirable.

[0030] The reaction of a carbonyl compound and living polyethylene is completed within about 1 minute also at a room temperature in a homogeneous system. However, when the molecular weight of polyethylene is generating precipitation highly, the reaction of several minutes - several hours is needed. Although there is especially no limit in reaction temperature, 0 degree C - 100 degrees C are usually preferably performed at 20 degrees C - 80 degrees C. It is carried out in the temperature same generally as the temperature used for the polymerization. Although not limited especially about the addition approach of a carbonyl compound, it is desirable to add, after diluting with the hydrocarbon solvent used for a polymerization [a minute amount every] from being accompanied by generation of heat.

[0031] In the manufacturing method of the polyethylene macro monomer which has an acryloyl (meta) radical at the end of this invention, it is also possible to replace with a reaction with the carbonyl compound like the above, and to perform oxygen acid-ization of a living end as a second stage story. After removing the ethylene gas in the reactor containing the living polyethylene which specifically reached predetermined molecular weight, it is attained by introducing oxygen. It is desirable to adjust a reaction rate using the oxygen diluted by suitable concentration depending on the reaction condition with inert gas, such as nitrogen and an argon. Generally this oxygen acid-ization is attained by introducing dry air. The introductory rate and pressure of oxygen (mixing) gas will not be restricted especially if it is the range which can control a reaction rate. In order to prevent generation of a peroxide, introducing a minute amount every is desirable. Although there is especially no limit also about the temperature at the time of performing an oxygen acid-ized reaction, -78 degrees C - 100 degrees C are usually -30 degrees C - 70 degrees C preferably.

[0032] Although the polyethylene generated even on the second stage story has the lithium alkoxide at the molecule end, it makes acrylic-acid (meta) halide, i.e., an acrylic acid, or a methacrylic acid react to the molecule end of the polyethylene obtained by the above-mentioned approach as the third step next. Although there is especially no limit in the amount of the acrylic-acid halide to add (meta), it is good to an alkoxide end at a 1 to 1.2 time mol equivalent grade. Although this reaction is slow compared with the reaction of a carbonyl compound and alkyl lithium, it is completed within several [about] minutes above a room temperature. However, when the molecular weight of an alkoxide becomes very large, the reaction on several [several hours -] is needed. Although there is especially no limit in reaction

temperature, 0 degree C - 100 degrees C are usually preferably performed at 20 degrees C - 80 degrees C. The same [as that of the temperature generally used at the pre-reaction] or it is carried out a little at an elevated temperature.

[0033]

[Effect of the Invention] By this invention, the new polyethylene macro monomer which has an acryloyl (meta) radical at the end can be obtained by high yield and the high grade. Since the polyethylene macro monomer obtained by this invention has an acryloyl radical at every (meta) one molecule end of almost all, it can compound the Kushigata graft polymer by copolymerizing with other various vinyl monomers. Moreover, this graft polymer is used suitable for the compatibilizer for polymer blends, a surface treatment agent, etc.

[0034]

[Example] An example is used for below and this invention is explained to it in more detail.

Into the 1l. autoclave which carried out the example 1 nitrogen purge, desiccation cyclohexane 400ml, tetramethylethylenediamine 3ml, and n-butyl lithium (1.6 mols/(l.)) 12.5ml were taught, and ethylene gas was introduced by the pressure of 2kg/cm² in 30 degrees C. After performing a polymerization for 30 minutes, the nitrogen purge of the ethylene gas was removed and carried out, and benzaldehyde 2.2ml was dropped there. After making it react for 5 minutes at 30 degrees C, methacrylic-acid chloride 2.2ml was dropped. After making it react for 15 minutes at 30 degrees C, the autoclave was opened and contents were supplied in the 2l. methanol. After agitating for 1 hour, the solid-states generated in filtration under reduced pressure were collected, it dried under the vacuum in 50-degree C oven for 24 hours, and the white solid-state was obtained. The number average molecular weight of a product was 730 as a result of the GPC analysis (it proofreads by alt.dichlorobenzene, 135 degrees C, and the polyethylene correlation sample) using the equipment of a 13.0g and the product made from Waters.

[yield / of a product]

[0035] One H-NMR analysis (the product made from Bruker, 200MHz, tetrachloroethylene, 80 degrees C.) DMSO-d₆ was used with the double pipe as a lock solvent, and TMS was used as an external standard. a result -- 0.8 ppm (triplet) -- an initiation end methyl group and near 1.2 ppm, the signal of a phenyl group was observed by the methylene group of a principal chain, and 2.0 ppm (double doublet) at the methyl of a methacryloyl radical, 5.5, and 6.2 ppm, and was observed by the vinyl of a methacryloyl radical, and 5.8 ppm (triplet) benzylic-position methine and near 7.2 ppm. The integral ratio of each signal showed that the rate of end methacryloyl radical installation was 87%.

[0036] After performing the polymerization of ethylene by the same approach as example 2 example 1, ethylene gas was removed and it permuted by dry air. After performing oxidation reaction for 10 minutes at 30 degrees C, methacrylic-acid chloride 2.2ml was added and it was made to react for 15 minutes. After treatment was performed like the example 1 and 12.8g of white solid-states was obtained. 670 (the same GPC as an example 1) and the rate of end methacryloyl radical installation of number average molecular weight were 80% (the same 1 H-NMR as an example 1).

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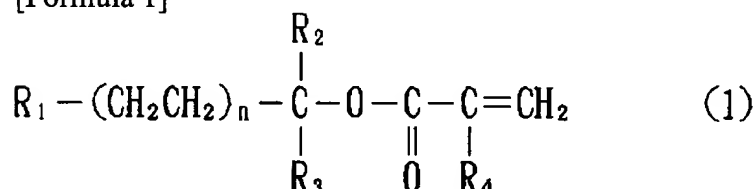
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CLAIMS

[Claim(s)]

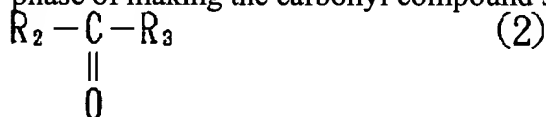
[Claim 1] The polyethylene macro monomer which is expressed with a degree type (1) and which has an acryloyl radical or a methacryloyl radical at the end.

[Formula 1]



(For R1, the straight chain of carbon numbers 1-6 or the saturated hydrocarbon radical of branching, and R2 and R3 are [hydrogen or a methyl group, and n of the aliphatic series of hydrogen or carbon numbers 1-18 or an aromatic hydrocarbon radical, and R4] the integers of 10-1000 among a formula, and even if R1-R3 are the same, they may differ.)

[Claim 2] 1) the phase of carrying out living polymerization of the ethylene using the straight chain of carbon numbers 1-6, or the alkyl lithium / the 3rd class diamine system initiator of branching, and the phase of making the carbonyl compound shown by 2 degree type (2) reacting -- and [Formula 2]



(R2 and R3 are the aliphatic series or aromatic hydrocarbon of hydrogen or carbon numbers 1-18 independently among a formula.)

3) The manufacturing method of the polyethylene macro monomer which has an acryloyl radical or a methacryloyl radical at the end which consists of a phase of making acrylic-acid halide or methacrylic-acid halide reacting.

[Claim 3] 1) The manufacturing method of the polyethylene macro monomer which has an acryloyl radical or a methacryloyl radical at the end which consists of a phase of carrying out living polymerization of the ethylene using the straight chain of carbon numbers 1-6, or the alkyl lithium / the 3rd class diamine system initiator of branching, and a phase of making the phase of performing 2 oxygen-acid-ization and 3 acrylic-acid halide, or methacrylic-acid halide reacting.

[Translation done.]

JAPANESE [JP,06-329720,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE
INVENTION TECHNICAL PROBLEM MEANS EXAMPLE

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EFFECT OF THE INVENTION

[Effect of the Invention] By this invention, the new polyethylene macro monomer which has an acryloyl (meta) radical at the end can be obtained by high yield and the high grade. Since the polyethylene macro monomer obtained by this invention has an acryloyl radical at every (meta) one molecule end of almost all, it can compound the Kushigata graft polymer by copolymerizing with other various vinyl monomers. Moreover, this graft polymer is used suitable for the compatibilizer for polymer blends, a surface treatment agent, etc.

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EXAMPLE

[Example] An example is used for below and this invention is explained to it in more detail. Into the 1l. autoclave which carried out the example 1 nitrogen purge, desiccation cyclohexane 400ml, tetramethylethylenediamine 3ml, and n-butyl lithium (1.6 mols/(l.)) 12.5ml were taught, and ethylene gas was introduced by the pressure of 2kg/cm² in 30 degrees C. After performing a polymerization for 30 minutes, the nitrogen purge of the ethylene gas was removed and carried out, and benzaldehyde 2.2ml was dropped there. After making it react for 5 minutes at 30 degrees C, methacrylic-acid chloride 2.2ml was dropped. After making it react for 15 minutes at 30 degrees C, the autoclave was opened and contents were supplied in the 2l. methanol. After agitating for 1 hour, the solid-states generated in filtration under reduced pressure were collected, it dried under the vacuum in 50-degree C oven for 24 hours, and the white solid-state was obtained. The number average molecular weight of a product was 730 as a result of the GPC analysis (it proofreads by alt.dichlorobenzene, 135 degrees C, and the polyethylene correlation sample) using the equipment of a 13.0g and the product made from Waters.

[yield / of a product]

[0035] One H-NMR analysis (the product made from Bruker, 200MHz, tetrachloroethylene, 80 degrees C.) DMSO-d₆ was used with the double pipe as a lock solvent, and TMS was used as an external standard. a result -- 0.8 ppm (triplet) -- an initiation end methyl group and near 1.2 ppm, the signal of a phenyl group was observed by the methylene group of a principal chain, and 2.0 ppm (double doublet) at the methyl of a methacryloyl radical, 5.5, and 6.2 ppm, and was observed by the vinyl of a methacryloyl radical, and 5.8 ppm (triplet) benzylic-position methine and near 7.2 ppm. The integral ratio of each signal showed that the rate of end methacryloyl radical installation was 87%.

[0036] After performing the polymerization of ethylene by the same approach as example 2 example 1, ethylene gas was removed and it permuted by dry air. After performing oxidation reaction for 10 minutes at 30 degrees C, methacrylic-acid chloride 2.2ml was added and it was made to react for 15 minutes. After treatment was performed like the example 1 and 12.8g of white solid-states was obtained. 670 (the same GPC as an example 1) and the rate of end methacryloyl radical installation of number average molecular weight were 80% (the same 1 H-NMR as an example 1).

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L3: Entry 2 of 2

File: DWPI

Nov 29, 1994

DERWENT-ACC-NO: 1995-048868

DERWENT-WEEK: 199507

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TITLE: New polyethylene@ macromonomer(s) - contg. (meth)acryloyl at one terminal
for blend polymer.

PATENT-ASSIGNEE: KAO CORP (KAOS)

PRIORITY-DATA: 1993JP-0122856 (May 25, 1993)

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PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
<input type="checkbox"/> JP 06329720 A	November 29, 1994		005	C08F008/24

APPLICATION-DATA:

PUB-NO	APPL-DATE	APPL-NO	DESCRIPTOR
JP 06329720A	May 25, 1993	1993JP-0122856	

INT-CL (IPC): C08F 8/24

ABSTRACTED-PUB-NO: JP 06329720A

BASIC-ABSTRACT:

New polyethylene macromonomers contg. (meth)acryloyl at one terminal are of formula (1), R1 is 1-6C satd. hydrocarbon gp. R2, R3 are H, or 1-18C aliphatic or aromatic hydrocarbon gp; R4 is H or methyl; and n is 10-1,000.

The prepn. of macromonomers comprises (1) living-polymerisation of ethylene, using an initiator of 1-6C alkyl lithium/tert. diamine, (2) reaction of carbonyl cpds. of formula R2(O)-R3 (2), or oxygen-oxidn. and (3) reaction of (meth)acrylic acid halide.

USE/ADVANTAGE - The new (meth)acryloyl-contg. polyethylene macromonomers are used as blend polymers or surface-improving agents.

ABSTRACTED-PUB-NO: JP 06329720A

EQUIVALENT-ABSTRACTS:

CHOSEN-DRAWING: Dwg.0/0

DERWENT-CLASS: A17

CPI-CODES: A04-G02D; A10-E07B;

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L3: Entry 1 of 2

File: JPAB

Nov 29, 1994

PUB-NO: JP406329720A

DOCUMENT-IDENTIFIER: JP 06329720 A

TITLE: POLYETHYLENE MACROMONOMER AND ITS PRODUCTION

PUBN-DATE: November 29, 1994

INVENTOR-INFORMATION:

NAME

COUNTRY

ITO, KOJI

NAKAMURA, GENICHI

AMIYA, TSUYOSHI

ASSIGNEE-INFORMATION:

NAME

COUNTRY

KAO CORP

APPL-NO: JP05122856

APPL-DATE: May 25, 1993

INT-CL (IPC): C08F 8/24

ABSTRACT:

PURPOSE: To produce, in a high yield, a new high-purity polyethylene macromonomer which has a terminal (meth)acryloyl group and can be copolymerized with another vinyl monomer to give a comb-type graft polymer suitable as a polymer blend compatibilizer, a surface modifier, etc.

CONSTITUTION: Ethylene is subjected to living polymn. using a 1-6C linear or branched alkylolithium/tert. diamine initiator, reacted with a specific carbonyl compd. or oxidized with oxygen, and reacted with a (meth)acrylic acid halide to give a polyethylene macromonomer of the formula (wherein R1 is a 1-6C linear or branched satd. hydrocarbon group; R2 and R3 are each H or a 1-18C aliph. or arom. hydrocarbon group provided R1, R2, and R3 are the same or different from each other; R4 is H or methyl; and n is an integer of 10-1,000).

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